

WE CLAIM:

1. A method of analyzing argentinated peptides or proteins using mass spectrometry comprising:
 - (a) combining an oligopeptide with silver to provide a sample comprising argentinated oligopeptide;
 - (b) submitting the sample to a mass spectrometer;
 - (c) performing scans of silver containing peaks in optimum collision energies;
 - (d) identifying any doublet or triplet peak pattern;
 - (e) confirming with Y ions;
 - (f) determining partial sequence by the mass separation between two successive doublet or triplet pattern.
2. A method according to claim 1 wherein the performing scans comprises collecting product ion spectra of the $[M + Ag]^+$ ion, where M = oligopeptide;
3. A method according to claim 1 or 2 wherein the oligopeptide comprises from about 3 to about 10 amino acids.
4. A method according to any one of claims 1-3 wherein the silver is silver nitrate.
- 20 5. A method according to anyone of claims 1-4 wherein the determination of partial sequence comprises searching for, and identifying cleaved amino acid residues based on differences in *m/z* values of neighboring triplets where the *m/z* value of the $[b_n - H + Ag]^+$ ion and the corresponding $[y_n + H + Ag]^+$ ion are related by the formula: $[y_n + H + Ag]^+ = [M + Ag]^+ + Ag^+ - [b_n - H + Ag]^+$.
- 25 6. A method according to claim 5 wherein the searching and identifying is conducted by a custom search algorithm.
7. A method according to claim 6 wherein the algorithm is written in

Visual Basic and looks for the triplet peak pattern of $(m/z)_1$, $(m/z)_2 = (m/z)_1 - 18.0$, and $(m/z)_3 = (m/z)_2 - 28.0$ as well as the doublet pattern of $(m/z)_2$ and $(m/z)_3$, all to within $\pm 0.5 m/z$ unit.

8. A method according to anyone of claims 1-7 wherein product ion
5 spectra of the $[M + Ag]^+$ ion are collected under $E_{cm}s$, of 1.5, 2.0, 2.5 and
3.0 eV.

9. A method according to anyone of claims 1-8 wherein the mass
spectrometer is a triple quadrupole mass spectrometer, two triple
10 quadrupole mass spectrometers, a quadrupole/time-of-flight mass
spectrometer, an ion-trap mass spectrometer, or a time-of-flight mass
spectrometer amenable to post-source decay or collision-induced
dissociation.

10. A method of analyzing argentinated peptides or proteins using
mass spectrometry comprising:

- 15 (a) combining an oligopeptide with silver nitrate in solution;
- (b) submitting a sample of the solution to a mass spectrometer;
- (c) collecting product ion spectra of the $[M + Ag]^+$ ion, where M
= oligopeptide;
- (d) identifying a triplet peak pattern;
- 20 (e) identifying a doublet peak pattern;
- (f) searching for, and identifying cleaved amino acid residues
based on differences in m/z values of neighboring triplets where the m/z
value of the $[b_n - H + Ag]^+$ ion and the corresponding $[y_n + H + Ag]^+$ ion
are related by the formula: $[y_n + H + Ag]^+ = [M + Ag]^+ + Ag^+ - [b_n - H +$
25 $Ag]^+$.

11. A method according to claim 10 wherein the oligopeptide
comprises from about 3 to about 10 amino acids.

12. A method according to claim 10 or 11 wherein the searching and
identifying is conducted by a custom search algorithm.

13. A method according to claim 12 wherein the algorithm is written in Visual Basic and looks for the triplet peak pattern of $(m/z)_1$, $(m/z)_2 = (m/z)_1 - 18.0$, and $(m/z)_3 = (m/z)_2 - 28.0$ as well as the doublet pattern of $(m/z)_2$ and $(m/z)_3$, all to within $\pm 0.5 m/z$ unit.
- 5 14. A method according to anyone of claims 10 to 13 wherein product ion spectra of the $[M + Ag]^+$ ion are collected under E_{cms} , of 1.5, 2.0, 2.5 and 3.0 eV.
- 10 15. A method according to anyone of claims 10-14 wherein the mass spectrometer is a triple quadrupole mass spectrometer, two triple quadrupole mass spectrometers, a quadrupole/time-of-flight mass spectrometer, an ion-trap mass spectrometer, or a time-of-flight mass spectrometer amenable to post-source decay or collision-induced dissociation.